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# OPTICAL RECORDING MEDIUM [Hikari kiroku baitai]

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### Claims

- 1. An optical recording medium, characterized by the fact that in an optical recording medium in which a reflective film is installed on a substrate, the reflective film consists of a thin film with a composition containing 70-99 at% Cu and 1-30 at% Al.
- 2. The optical recording medium of Claim 1, characterized by the fact that the above-mentioned reflective film consists of the above-mentioned thin film with a composition further containing 0.1-10 at% of at least one kind of element being selected from Fe, Ni, and Mn.
- 3. The optical recording medium of Claim 2, characterized by the fact that the above-mentioned reflective film consists of the above-mentioned thin film with a composition containing 70-90 at% Cu, 1-20 at% Al, and 0.5-10 at% of at least one of Fe and Ni (however, the total amount of Fe and Ni does not exceed 10 at%).
- 4. The optical recording medium of Claim 2, characterized by the fact that the above-mentioned reflective film consists of the above-mentioned thin film with a composition containing 70-90 at% Cu, 1-20 at% Al, and 0.1-5 at% Mn.
- 5. The optical recording medium of Claim 2, characterized by the fact that the above-mentioned reflective film consists of the above-mentioned thin film with a composition containing 70-90 at% Cu, 5-15 at% Al, 1-8 at% Fe, 0.5-7 at% Ni, and 0.1-5 at% Mn (however, the total amount of Fe and Mn does not exceed 10 at%).
- 6. The optical recording medium of any of Claims 1-5, characterized by the fact that the reflective film consists of a thin film with a composition in which the total content of Cu, Al, Fe, Ni, and Mn is 98 atomic mol%.

7. The optical recording medium of any of Claims 1-6, characterized by the fact that a pigment film as a recording layer is installed in the middle of the above-mentioned substrate and the above-mentioned reflective film.

8. The optical recording medium of any of Claims 1-6, characterized by the fact that several pits are formed on the above-mentioned substrate; and information can be read out by light through these pits.

## Detailed explanation of the invention

[0001]

Technical field of the invention

The present invention pertains to an optical recording medium having a reflective film with high reflectance and excellent corrosion resistance.

[0002]

Prior art

Optical recording media provided with a recordable area capable of a direct recording on a disk, for example, recordable compact disks can carry out recording, and after recording, they can be reproduced by compact disk players, drives, etc., for reproduction.

[0003]

In a CD-R reflective film as a kind of the above-mentioned recordable compact disk, Au or an alloy mainly composed of Au is used. The reflective film formed of Au or an alloy having Au as its main component can realize a high reflectance of 65% or more at a laser wavelength of 780 nm for reading out recorded information, even if a pigment recording layer exists, and also has high corrosion

resistance. However, since the reflective film formed of Au or an alloy mainly composed of Au is expensive, the cost of the above-mentioned CD-R is raised.

#### [0004]

On the other hand, in case an inexpensive metal such as Ag, Cu, and Al and an alloy mainly composed of them are used as a reflective film, since the corrosion resistance is inferior, the change in the performances of a disk such as a decrease in the reflectance and increase of errors due to the corrosion is caused with time.

## [0005]

In Japanese Kokai Patent Application No. Hei 2[1990]-128332, an information recording medium having a thin film mainly composed of at least one kind being selected from a group comprised of Al, Cu, Ag, and Au and at least one kind being selected from an element group including Ti, Fe, Ni, etc., in contact with a protective layer close to or adjacent to a thin film for information recording that generates a phase change by receiving the irradiation of beams for recording is presented. However, in said invention, it is confirmed that the gold system alloy is best, and a reflective film formed of Cu and Al is neither substantially presented nor hinted at.

#### [0006]

In reflective films of compact disks (hereinafter, also called CD) such as CD-Audio and CD-ROM being manufactured by transferring pits to a substrate through a mold, since a significantly high reflectance is not required in terms of structure, Al is usually used.

[0007]

However, for example, in optical disks such as CD-R having an organic pigment as a recording film, since light is absorbed by said pigment, a reflective film with a reflectance higher than that of the above-mentioned compact disks is required, and as mentioned above, Au is usually used as a reflective film in CD-R. If only the reflectance is considered, Ag has a reflectance higher than that of Au. However, since Au is inferior in corrosion resistance compared with Au, and the reflectance is lowered over time, the reflective film formed of only Ag is inappropriate as a reflective film of CD-R. After all, an expensive Au is still used as a reflective film of CD-R in practice.

[8000]

Problems to be solved by the invention

Therefore, the purpose of the present invention is to provide an optical recording medium having a high reflectance reflective film and excellent corrosion resistance at low cost.

[0009]

Means to solve the problems

The present inventors researched the above problems in earnest to achieve the above-mentioned purpose, and as a result, it was unexpectedly discovered that a thin film containing a specific ratio of Al to Cu content had high reflectance and excellent corrosion resistance. The present invention is based on the above-mentioned knowledge, and the above-mentioned purpose is achieved by providing an optical recording medium characterized by the fact that in an optical recording medium in which a reflective film is installed on a substrate, the reflective film consists of a thin film with a composition containing 70-99 at% Cu and 1-30 at% Al.

## [0010]

It has not been known that the above-mentioned thin film renders a reflective film for an optical recording medium with excellent corrosion resistance and high reflectance, and this fact was surprising. Also, the reflective film with the above-mentioned constitution exhibits a color similar to gold and renders an aesthetically excellent optical recording medium. The optical recording medium of the present invention is explained in detail below.

## [00011]

# Embodiments of the invention

The optical recording medium of the present invention has a structure in which a reflective film is installed on a substrate and includes a medium that can record information by light, a medium that can read out a recorded information by light, a medium that erases a record or rewrite a record by light, etc.

#### [0012]

As detailed examples of the optical recording medium, recordable optical disks (CD-R) having a thin pigment film as a recording layer, compact disks (CD) in which information is recorded by pits formed on a substrate and the recorded information can be read out by light, photomagnetic disks (MD or MO) capable of erasing or rewriting records, phase change type optical disks (PD, CD-E), etc., can be mentioned.

#### [0013]

First, a recordable compact disk (CD-R) as one pattern of the optical recording medium of the present invention is explained referring to Figure 1. Figure 1 is a schematic cross section in the radial direction of the CD-R, and pigment film 4 as a recording layer, reflective film 3, and protective film 5 are laminated in this sequence on a substrate transparent to the light being used.

## [0014]

As a material for forming the substrate 2, plastics such as polycarbonate and methyl polymethacrylate and glasses can be mentioned. Among them, polycarbonate is preferable. The thickness of the substrate 2 is usually 1.2 mm. Then, a spiral guide groove 6 used as a laser irradiation guide is usually installed.

## [0015]

As pigments of the pigment film 4, any pigment in which the optical constant is changed by absorbing light, for example laser energy, is used without particular limitation. Specifically, cyan group pigment, squalylium [transliteration] group pigment, chlokonium group pigment, azulenium group pigment, triarylamine pigment, anthraquinone group pigment, azo group pigment containing a metal, dithol metal complex salt group pigment, indoaniline metal complex group pigment, phthalocyanine group pigment, phthalocyanine group pigment, intermolecular CT complex group pigment, etc., are appropriately used. They can be used alone or in combination. Also, antioxidant, binder, etc., can be added to the pigment film 4.

#### [0016]

As a method for forming the pigment film 4 containing an organic pigment, a method that dissolves an organic pigment in an organic solvent and spin-coats it on a transparent substrate 2 is preferably employed, however a vapor deposition method can also be employed for sublimation pigments such as

phthalocyanine group pigment. The thickness of the pigment film 4 is appropriately selected in accordance with the wavelength being used, the optical properties of the reflective film 3, the material of the pigment film 4, etc., in consideration of recording density, performance coefficient, etc., for an optical energy being used for recording such as laser, and the film thickness is usually in a range of 120-150 nm.

### [0017]

The reflective film 3 in the present invention consists of a thin film with a composition containing 70-99 wt% Cu and 1-30 wt% Al. The above-mentioned specified composition range of the thin film is important for rendering a reflective film with high reflectance and corrosion resistance, and the above-mentioned characteristics become excellent by satisfying the above-mentioned composition. If the Cu content is more than 99 at% or the Al content is less than 1 at%, the corrosion resistance is lowered, and if the Cu content is less than 70 at% or the Al content is more than 30 at%, the reflectance is lowered.

#### [0018]

Also, in terms of corrosion resistance improvement, it is preferable for said thin film to include 0.1-10 at% at least one kind of element being selected from Fe, Ni, and Mn. Also, it is further preferable to include all [three] of Fe, Ni, and Mn. Then, as the composition of the thin film, the total content of Cu, Al, Fe, Ni, and Mn is preferably 98 at% or more, more preferably 99 at% or more in terms of reflectance and corrosion resistance. In other words, the thin film constituting the reflective film in the present invention can include elements such as gold, platinum, palladium, titanium, molybdenum, tantalum, zirconium, vanadium, and tungsten other than Cu, Al, Fe, Ni, and Mn in the range where the

purpose of the present invention is not damaged, and the total amount of these elements is preferably 2 at% or less, more preferably 1 at% or less.

#### [0019]

As preferable compositions of the thin film constituting the reflective film, the following (i)-(iv) can be mentioned.

- (i) A composition containing 75-95 at% Cu and 5-25 at% Al.
- (ii) A composition containing 75-90 at% Cu, 1-17 at% Al, and 0.5-8 at% at least one of Fe and Ni (however, the total amount of Fe and Ni does not exceed 8 at%).
  - (iii) A composition containing 75-90 at% Cu, 5-17 at% Al, and 0.5-8 at% Mn.
- (iv) A composition containing 70-90 at% Cu, 5-15 at% Al, 1-8 at% Fe, 0.5-7 at% Ni, and 0.1-5 at% Mn (however, the total amount of Fe and Mn does not exceed 10 at%).

Among the thin films with the above-mentioned compositions (i)-(iv), the thin films with the compositions (ii)-(iv) are preferable in terms of excellent corrosion resistance of the reflective film, and the thin films with the composition (iv) are especially preferable in rendering a high corrosion resistance to the reflective film.

#### [0020]

Also, the thin film constituting the above-mentioned reflective film of the present invention may be any of an alloy pattern of each metal component (the alloy in the present invention means an alloy designated in the alloy item of Iwanami Physiochemical Dictionary (3<sup>rd</sup> enlarged edition published on February 24, 1981)), a mixture pattern of each metal component, or a pattern in which a thin film

composed of elements of each metal component is laminated. Also, a pattern in which these patterns are combined may be adopted, however the formation of a thin film by a vapor deposition method is simple.

## [0021]

The above-mentioned reflective film 3 can be formed directly or via other films on the above-mentioned pigment film 4 by its well-known sputtering method and vacuum deposition method. The thickness of the above-mentioned reflective film 3 is preferably 50-150 nm.

# [0022]

Furthermore, if necessary, a surface treatment may also be applied to the surface of the above-mentioned reflective film 3 by a surface treatment agent such as a triazinethiol group compound.

# [0023]

As the protective film 5 being formed on the above-mentioned reflective film 3, a hard material such as acrylic ultraviolet-curable resin is appropriately used, and usually, the protective film can be formed by spreading at a thickness of 2-20 m on the reflective film by a spin-coating method and curing by ultraviolet irradiation.

#### [0024]

Next, a compact disk (CD) as another embodiment of the optical recording medium of the present invention in which information is recorded by the combination of several pits formed on a substrate and said recorded information is read out by lights is explained referring to Figure 2. Figure 2 is a schematic

cross section in the track direction of CD, and a reflective film 3 and a protective film 5 are laminated in this sequence on a transparent substrate 2 to lights being used.

#### [0025]

As materials for forming the above-mentioned substrate 2, the materials described for CD-R can be used, and polycarbonate is preferable. The thickness of the substrate 2 is the thickness described for CD-R. On the above-mentioned substrate, several pits 7 exist, and information is recorded by these pits.

## [0026]

As the composition of the reflective film 3, the thickness of the reflective film, the method for forming the reflective film, etc., those described for CD-R including preferable patterns can be applied. Furthermore, as the protective film, the protective film described for CD-R can also be applied.

### [0027]

In the above-mentioned optical recording medium of the present invention explained above, since the reflectance of the above-mentioned reflective film is large enough to meet the CD-R standards, a high output is obtained at a time of readout. Thus, the selection width of a pigment for CD-R, for instance, is widened in designing the optical recording medium. Also, even in case the CD drive is designed, the selection width of the kinds of laser beams being used during readout is widened, and even if the power of laser beams is more or less lowered for a certain reason, it can be continuously used, so that advantages in terms of design can be generated. Also, since the above-mentioned reflective film is excellent in the corrosion resistance, the decrease of the reflectance and the increase of the generation of

readout errors with a lapse of time are suppressed. Furthermore, since the above-mentioned reflective film is inexpensive, the contribution to the cost reduction of the optical recording medium is great.

[0028]

## Application examples

Next, the present invention is explained in detail by application examples, however the present invention is not limited to these application examples.

# Application Example 1

# (1) Preparation of CD-R

As a transparent substrate, a polycarbonate substrate with a diameter of 120 mm and a thickness of 1.2 mm on which periodically serpentine tracking grooves (guide grooves) were installed was used for a recordable compact disk (CD-R).

A cyanine pigment represented by the following structural formula (1)

[0029]

# Structure 1

## [0030]

was dissolved at 2.2 wt% (to the solvent wt%) in a methyl cellosolve solvent, filtered, and spread on the above-mentioned substrate by a spin-coating method. After spreading, it was dried for 10 min in an oven at 80°C to completely evaporate the solvent in the pigment film, so that a pigment film was formed. The thickness of the pigment film was set to 120 nm. Next, a Cu-Al-Fe-Mn thin film with a thickness of 100 nm (83 at% Cu content, 11 at% Al content, 4 at% Fe content, 1 at% Ni content, and 1 at% Mn content) was formed as a reflective film on the pigment film by a brush vapor deposition method using a resistance heating crucible. Furthermore, an ultraviolet-curable resin SD-1700 (made by Dainippon Ink and Chemicals, Inc.) was spread at a thickness of 3 μm on the reflective film by the spin-coating method and cured by irradiating ultraviolet rays from an ultraviolet irradiator, so that a protective film was formed. Thereby, a CD-R was prepared.

# [0031]

## (2) Performance evaluation of CD-R

EFM signals were recorded on the CD-R obtained by an optical disk evaluator DDU-1000 (made by Pulse Tech Co.). Next, the CD-R recorded was held for 1000 h under the environment of a temperature of 80°C and a humidity of 90% RH. Before and after holding this disk under the high-temperature and high-humidity environment, the reflectance and the C1 error (the average number of error generated per 1 sec) were measured. The results are shown in Table 1.

## [0032]

# Application Examples 2-5 and Comparative Examples 1-4

Application Example 1 except for using the compositions shown in Table 1 as reflective films was repeated. The performances of CD-R prepared are shown in Table 1.

[0033]

					2	3					
			① 反射無關係					度射率 第一份		C 1 エラ … (学術発力(数数)	
		1	Cu	AI	Pε	Ni	Mn	<b>#</b> 5	<sup>8</sup> (7)	ී	*(7)
		1	8.8	11	4	ş	1	63	68	*	11
4	寒	2	8.0	5	\$	3	8	8 5	6.0	2	17
	84	3	75	15	7	2	L	88	5.7	3	8
	8	4	3.5	20	\$	8	9	6.9	55	2	LS
		5	73	10	0	4	3	6.8	65	3	3.8
(5)	ě	1	5.8	2.0	10	6.1	5	4.8	47	A	
		2	180	0	0	8	8	7.8	57	2	236
9	85	3	Ay=159				73	8.0	2	226	
	Ľ	4	8 5	5	15	8	8	6.8	52	5	236

Note): 1) Before holding under the high-temperature and high-humidity environment

- 2) After holding under the high-temperature and high-humidity environment
- Key: 1 Reflective film composition (at%)
  - 2 Reflectance (%)
  - 3 C1 error (average number of error generated)
  - 4 Application Example
  - 5 Comparative Example
  - 6 Before<sup>1)</sup>

7 After<sup>2)</sup>

[0034]

From the results of Table 1, the following facts (1)-(3) are apparent.

- (1) In CD-R having the reflective film with the composition specified in the present invention, (i) the reflectance is high, and even if this disk is held for a long time under a high-temperature and high-humidity environment, the reflectance can be maintained at high level. (ii) The number of C1 error being generated is not considerably increased, even if this disk is held for a long time under the above-mentioned environment.
- (2) In CD-R (Comparative Example 1) having the reflective film with a composition out of the range specified in the present invention, (i) the reflectance is quite low, and even the corrosion resistance test could not be tried.
- (3) In CD-R (Comparative Examples 2 and 3) having reflective films formed of Cu or Ag, the initial reflectance is high. However, if these disks are held for a long term under a high-temperature and high-humidity environment, the reflectance is considerably lowered, and the number of C1 error being generated is considerably increased.

The above facts mean that the reflective film with a specific composition used in the optical recording medium of the present invention has high reflectance and excellent corrosion resistance.

## [0035]

### Effect of the invention

According to the present invention, an optical recording medium with high reflectance and excellent corrosion resistance can be provided at low cost. Also, the above-mention reflective film exhibits a color similar to gold, and an aesthetically excellent optical recording medium can be obtained.

## [0036]

# Brief description of the figures

Figure 1 is a schematic cross section in the radial direction of CD-R.

Figure 2 is a schematic cross section in the track direction of CD.

# Explanation of symbols

- 1 CD-R
- Substrate
- 3 Reflective film
- 4 Pigment film
- 5 Protective film
- 6 Guide groove
- 7 Pit
- 11 CD



Figure 1

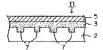


Figure 2